

## X-Ray Crystal Structures of two Pyrethroid Insecticides: *cis*-3-Phenoxybenzyl 3-(2,2-Dibromovinyl)-2,2-dimethylcyclopropanecarboxylate and the 3-(2,2-Dichlorovinyl) Analogue

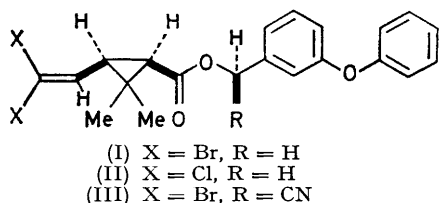
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The crystal structures of two isomorphous crystalline pyrethroid insecticides have been determined by X-ray diffraction analysis. Both compounds crystallise in the orthorhombic space group  $P2_12_12_1$  with  $Z = 4$ . The bromo-compound (I) has cell dimensions  $a = 12.177(4)$ ,  $b = 26.707(9)$ , and  $c = 6.146(5)$  Å. The structure was solved by heavy-atom methods from diffractometer intensity data, and refined to  $R$  0.044 for 721 observed reflections. The absolute configuration was determined and confirmed the chemical work. The chloro-compound (II) has cell dimensions  $a = 12.168(16)$ ,  $b = 26.577(22)$ , and  $c = 6.006(4)$  Å. Intensity data were collected from films scanned on a microdensitometer, and the structure refined to  $R$  0.069 for 545 observed reflections.

The conformations of the two compounds are compared with each other and with those of other known pyrethroid structures in the crystalline state.

INSECTICIDAL activity in pyrethroids is related to molecular shape,<sup>1</sup> and refinement of such concepts requires a good basis of reliable information on molecular dimensions, configuration, and conformation. As part of this work I report the determination of the structures of (1*R*,3*R*)-*cis*-3-phenoxybenzyl 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate (I) (NRDC 157), and the 3-(2,2-dichlorovinyl) compound (II) (NRDC 167) in the solid state by X-ray diffraction analysis.

Compounds (I) and (II) are highly insecticidal members of a group of photostable pyrethroids.<sup>2</sup> The compound (III) (NRDC 161) is a further member of this group and its crystal structure has recently been reported.<sup>3</sup> The three compounds (I)—(III) all crystallise in the same space group and have similar cell dimensions. However, (I) and (II) have similar diffraction patterns, whereas that of (III) is different. We decided to solve the structure of (I), to compare and contrast it with that of (III), and of (II), to show any differences which



may have been introduced by substituting chlorine atoms for bromine.

The solution of these structures brings the number of pyrethroids whose crystal structures have been determined to four. The structure of the 6-bromo-2,4-dinitrophenylhydrazone derivative of (4*S*)-2-(prop-2-enyl)-rethron-4-yl (1*R*,3*R*)-*trans*-chrysanthemate [(*S*)-bioallethrin]<sup>4</sup> has been determined and was compared with that of (III) in ref. 3.

The crystal structure of (I) was solved by Patterson and Fourier methods and refined by least-squares techniques.

<sup>1</sup> M. Elliott, *Chem. and Ind.*, 1969, 776; *Bull. World Health Organisation*, 1971, **44**, 315; M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, and D. A. Pulman, *Proc. Amer. Chem. Soc. Symposium Mechanism of Pesticide Action: Cellular and Model Systems*, Los Angeles, California, April 1974, p. 80.

The absolute configuration was obtained by calculating structure factors (using anomalous dispersion coefficients for the bromine atoms) for the  $hkl$  and  $h\bar{k}l$  Bijvoet pairs. The resulting atomic co-ordinates appear in Table I and the atom numbering in Figure 1.

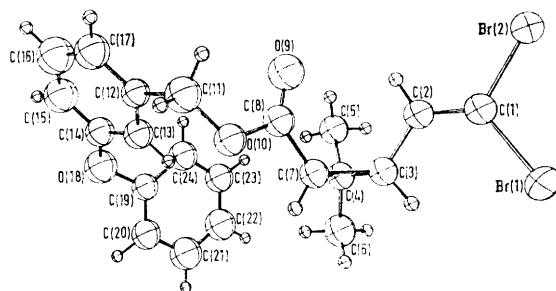


FIGURE 1 Molecule of (I) showing atom numbering system used. Hydrogen atoms are numbered according to the carbon atom to which they are bonded

The final atomic co-ordinates for (I) were used as a starting point for the refinement of the structure of (II) by least-squares methods. The absolute configuration of (II) was not established by this structure determination, but chemical and biological evidence indicates it to be the same as that of (I).<sup>2</sup> Final atomic co-ordinates appear in Table 2.

*The Structure of (I).*—The crystal structure results from the packing of discrete molecules: the closest intermolecular contacts are between hydrogen atoms and are all  $>2.68$  Å (Table 3). The packing diagram (Figure 2) shows there are no obvious strong interactions (such as hydrogen bonds) holding the molecules together in the crystal.

The isomer giving the lowest  $R$  (see Experimental section) also showed the same configuration about the two asymmetric centres on the cyclopropane ring as that known to be present from the method of synthesis.<sup>2</sup>

<sup>2</sup> M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, D. A. Pulman, and J. H. Stevenson, *Nature*, 1973, **246**, 169; P. E. Burt, M. Elliott, A. W. Farnham, N. F. Janes, and D. A. Pulman, *Pesticide Sci.*, 1974, **5**, 791; M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, and D. A. Pulman, *ibid.*, 1975, **6**, 537.

<sup>3</sup> J. D. Owen, *J.C.S. Perkin I*, 1975, 1865.

<sup>4</sup> M. J. Begley, L. Crombie, D. J. Simmonds, and D. A. Whiting, *J.C.S. Perkin I*, 1974, 1230.

Table 3 shows the bond lengths and angles. The only unusual feature of these is the short phenyl carbon-carbon distances, mean 1.363(8) Å; the mean phenyl

contact is 2.61 Å (Table 3) in this case. The absolute configuration is known to be (1*R*,3*R*)*cis*,<sup>2</sup> the same as that found for (I), although there is no crystallographic evidence for this in the present work.

The bond lengths and angles have estimated standard deviations which are slightly higher overall than those for (I), in line with the smaller number of observations used in the least-squares refinement. Again the phenyl carbon-carbon bond lengths are short [mean of 1.359(9) Å]; mean phenyl angles are 119.9(6)°. The cyclopropane ring has a mean bond length of 1.487(4) Å.

TABLE 1

Fractional co-ordinates for (I) ( $\times 10^4$ ) and isotropic vibration parameters ( $U_{\text{iso}} \times 10^3 \text{ \AA}^2$ ), with standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}$
Br(1)	-0 343(2)	-1 106(1)	9 843(3)	*
Br(2)	-0 723(1)	-1 565(1)	5 193(3)	*
C(1)	-0 533(11)	-0 974(5)	6 846(25)	42(4)
C(2)	-0 541(11)	-0 530(5)	5 994(22)	41(4)
C(3)	-0 406(12)	-0 049(5)	7 215(24)	41(4)
C(4)	-0 944(12)	0 429(5)	6 531(25)	44(4)
C(5)	-1 693(12)	0 429(5)	4 549(28)	55(4)
C(6)	-1 323(14)	0 773(6)	8 329(29)	62(5)
C(7)	0 265(13)	0 382(5)	6 245(24)	44(4)
C(8)	0 823(13)	0 325(6)	4 131(25)	51(5)
O(9)	0 482(9)	0 133(4)	2 554(19)	71(4)
O(10)	1 813(8)	0 556(3)	4 228(16)	50(3)
C(11)	2 426(13)	0 600(6)	2 298(29)	62(5)
C(12)	2 253(13)	1 079(5)	1 041(25)	43(5)
C(13)	1 626(12)	1 452(5)	1 980(25)	52(5)
C(14)	1 523(13)	1 904(6)	0 867(27)	56(5)
C(15)	2 032(17)	1 978(7)	-1 068(32)	77(6)
C(16)	2 627(16)	1 603(7)	-1 955(35)	85(6)
C(17)	2 745(15)	1 153(6)	-0 925(29)	68(6)
O(18)	0 928(10)	2 306(4)	1 724(21)	79(4)
C(19)	0 034(13)	2 223(6)	3 092(27)	53(5)
C(20)	-0 033(13)	2 475(5)	4 914(36)	65(4)
C(21)	-0 927(16)	2 425(7)	6 272(33)	83(6)
C(22)	-1 744(16)	2 128(7)	5 686(33)	81(6)
C(23)	-1 719(15)	1 883(6)	3 780(31)	67(6)
C(24)	-0 833(15)	1 912(6)	2 400(30)	67(5)
H(2)	-0 617	-0 497	4 469	
H(3)	-0 361	-0 140	8 643	
HA(5)	-2 389	0 265	4 959	
HB(5)	-1 373	0 244	3 414	
HC(5)	-1 856	0 765	4 144	
HA(6)	-0 823	0 755	9 496	
HB(6)	-2 052	0 682	8 756	
HC(6)	-1 329	1 115	7 760	
H(7)	0 720	0 577	7 118	
HA(11)	2 264	0 325	1 368	
HB(11)	3 201	0 588	2 680	
H(13)	1 263	1 394	3 365	
H(15)	1 989	2 297	-1 795	
H(16)	2 982	1 659	-3 351	
H(17)	3 147	0 887	-1 600	
H(20)	0 555	2 707	5 297	
H(21)	-0 958	2 622	7 605	
H(22)	-2 365	2 095	6 646	
H(23)	-2 355	1 676	3 411	
H(24)	-0 812	1 723	1 068	

\* Anisotropic vibration parameters ( $U_{ij} \times 10^4 \text{ \AA}^2$ ) in the expression:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + U_{22}h^2b^{*2} + 2U_{13}hla^*c^* + U_{33}l^2c^{*2} + 2U_{23}hkb^*c^*)]$ , with values:

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Br(1)	1 010(14)	493(11)	375(11)	-4(9)	-138(13)	83(10)
Br(2)	799(12)	429(10)	425(11)	-96(8)	35(12)	-5(10)

angles are 119.9(5)°. The cyclopropane ring has a mean bond length of 1.51(1) Å.

The conformation of (I) is described by the torsion angles and mean planes in Table 4, and is very different from that of (III), in spite of the similar cell dimensions and identical space group.

*The Structure of (II).*—The crystal structure, molecular conformation, and bond lengths and angles are very similar to those of (I). The minimum intermolecular

TABLE 2

Fractional co-ordinates for (II) ( $\times 10^4$ ) and isotropic vibration parameters ( $U_{\text{iso}} \times 10^3 \text{ \AA}^2$ )

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}$
Cl(1)	-0 398(5)	-1 104(2)	9 720(9)	*
Cl(2)	-0 745(4)	-1 158(2)	5 348(8)	*
C(1)	-0 577(12)	-1 003(5)	6 930(26)	38(4)
C(2)	-0 551(13)	-0 531(6)	6 106(27)	55(5)
C(3)	-0 427(14)	-0 055(6)	7 339(27)	52(5)
C(4)	-0 964(15)	0 419(6)	6 633(28)	44(5)
C(5)	-1 679(16)	0 433(7)	4 642(33)	70(6)
C(6)	-1 331(16)	0 773(7)	8 488(34)	71(6)
C(7)	0 249(15)	0 370(6)	6 457(28)	49(5)
C(8)	0 828(16)	0 326(6)	4 266(32)	61(6)
O(9)	0 535(10)	0 121(5)	2 652(22)	74(4)
O(10)	1 821(9)	0 567(4)	4 392(19)	60(4)
C(11)	2 452(15)	0 602(6)	2 376(33)	64(6)
C(12)	2 279(14)	1 082(6)	1 190(29)	49(5)
C(13)	1 612(14)	1 465(7)	2 023(29)	56(5)
C(14)	1 510(17)	1 902(7)	0 819(31)	64(6)
C(15)	2 045(16)	1 973(7)	-1 071(33)	66(6)
C(16)	2 682(17)	1 614(8)	-1 911(36)	77(6)
C(17)	2 797(16)	1 173(7)	-0 825(34)	70(6)
O(18)	0 902(12)	2 303(5)	1 601(25)	91(5)
C(19)	0 000(16)	2 238(6)	3 098(33)	58(5)
C(20)	-0 023(18)	2 495(7)	4 951(42)	73(5)
C(21)	-0 899(20)	2 455(8)	6 344(37)	86(7)
C(22)	-1 737(20)	2 147(8)	5 843(38)	90(7)
C(23)	-1 722(18)	1 886(7)	3 918(35)	73(6)
C(24)	-0 862(19)	1 915(7)	2 448(35)	78(6)
H(2)	-0 642	-0 501	4 523	
H(3)	-0 410	-0 133	8 826	
HA(5)	-2 354	0 284	5 053	
HB(5)	-1 329	0 243	3 965	
HC(5)	-1 750	0 776	4 226	
HA(6)	-0 781	0 772	9 652	
HB(6)	-2 019	0 660	9 012	
HC(6)	-1 372	1 108	7 861	
H(7)	0 708	0 552	7 394	
HA(11)	2 251	0 329	1 422	
HB(11)	3 216	0 574	2 755	
H(13)	1 232	1 423	3 421	
H(15)	1 966	2 293	-1 835	
H(16)	3 048	1 668	-3 308	
H(17)	3 249	0 918	-1 495	
H(20)	0 572	2 704	5 374	
H(21)	-0 932	2 650	7 692	
H(22)	-2 352	2 111	6 854	
H(23)	-2 327	1 670	3 555	
H(24)	-0 854	1 727	1 062	

\* Anisotropic thermal parameters (see Table 1), with values:

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Cl(1)	1 143(47)	565(31)	567(35)	11(31)	-147(40)	81(28)
Cl(2)	841(37)	420(23)	706(36)	-73(29)	-5(34)	-90(29)

The conformation of (II) (Table 4) is not significantly different from that of (I), in spite of the smaller size of the chlorine atoms.

TABLE 3

Bond lengths (Å), angles (°), and intermolecular contacts (Å) for (I) and (II)

(a) Bond lengths, with standard deviations in parentheses

	(I)	(II)
X(1)-C(1)	1.890(15)	1.711(17)
X(2)-C(1)	1.891(15)	1.678(15)
C(1)-C(2)	1.297(17)	1.350(19)
C(2)-C(3)	1.496(18)	1.474(22)
C(3)-C(4)	1.496(19)	1.481(21)
C(3)-C(7)	1.534(20)	1.493(22)
C(4)-C(5)	1.522(21)	1.480(23)
C(4)-C(6)	1.509(20)	1.534(22)
C(4)-C(7)	1.488(21)	1.486(23)
C(7)-C(8)	1.474(21)	1.497(23)
C(8)-O(9)	1.172(17)	1.167(19)
C(8)-O(10)	1.356(17)	1.369(19)
O(10)-C(11)	1.407(18)	1.437(21)
C(11)-C(12)	1.510(20)	1.476(22)
C(12)-C(13)	1.381(19)	1.395(20)
C(12)-C(17)	1.363(21)	1.386(22)
C(13)-C(14)	1.394(19)	1.373(22)
C(14)-O(18)	1.399(18)	1.382(20)
C(14)-C(15)	1.356(22)	1.322(23)
C(15)-C(16)	1.352(23)	1.328(24)
C(16)-C(17)	1.365(22)	1.348(24)
O(18)-C(19)	1.393(19)	1.429(20)
C(19)-C(20)	1.309(23)	1.307(25)
C(19)-C(24)	1.409(21)	1.410(23)
C(20)-C(21)	1.378(24)	1.359(27)
C(21)-C(22)	1.323(23)	1.343(27)
C(22)-C(23)	1.342(23)	1.347(26)
C(23)-C(24)	1.374(23)	1.371(25)

(b) Bond angles, with standard deviations in parentheses

	(I)	(II)
X(1)-C(1)-X(2)	112.6(8)	116.2(9)
X(1)-C(1)-C(2)	124.4(11)	120.1(13)
X(2)-C(1)-C(2)	123.1(12)	123.6(13)
C(1)-C(2)-C(3)	125.6(13)	128.1(16)
C(2)-C(3)-C(4)	123.0(12)	122.7(15)
C(2)-C(3)-C(7)	120.6(12)	121.8(15)
C(4)-C(3)-C(7)	58.8(9)	60.0(11)
C(3)-C(4)-C(5)	119.1(13)	120.9(15)
C(3)-C(4)-C(6)	116.6(12)	116.8(14)
C(3)-C(4)-C(7)	61.9(10)	60.4(11)
C(5)-C(4)-C(6)	113.8(12)	113.5(14)
C(5)-C(4)-C(7)	119.9(14)	121.9(15)
C(6)-C(4)-C(7)	116.1(14)	113.3(15)
C(3)-C(7)-C(4)	59.3(9)	59.6(10)
C(3)-C(7)-C(8)	120.7(13)	120.9(15)
C(4)-C(7)-C(8)	124.6(14)	122.5(16)
C(7)-C(8)-O(9)	127.7(15)	128.5(18)
C(7)-C(8)-O(10)	108.9(13)	109.3(15)
O(9)-C(8)-O(10)	123.4(14)	122.2(18)
C(8)-O(10)-C(11)	118.2(12)	117.1(14)
O(10)-C(11)-C(12)	115.3(13)	112.7(15)
C(11)-C(12)-C(13)	113.3(14)	122.7(17)
C(11)-C(12)-C(17)	121.1(15)	120.5(17)
C(13)-C(12)-C(17)	120.6(15)	116.8(17)
C(12)-C(13)-C(14)	118.0(15)	118.7(17)
C(13)-C(14)-C(15)	121.1(17)	121.9(20)
C(13)-C(14)-O(18)	121.8(14)	121.5(18)
C(15)-C(14)-O(18)	117.0(16)	116.5(19)
C(14)-C(15)-C(16)	119.3(19)	120.7(21)
C(15)-C(16)-C(17)	121.4(19)	120.1(20)
C(12)-C(17)-C(16)	119.6(17)	121.8(20)
C(14)-O(18)-C(19)	120.6(12)	122.1(15)
O(18)-C(19)-C(20)	118.8(15)	119.2(18)
O(18)-C(19)-C(24)	119.8(15)	118.1(17)
C(20)-C(19)-C(24)	121.0(16)	122.6(19)
C(19)-C(20)-C(21)	121.2(16)	120.0(20)
C(20)-C(21)-C(22)	119.1(18)	120.3(21)
C(21)-C(22)-C(23)	120.9(20)	119.7(23)
C(22)-C(23)-C(24)	122.0(18)	122.3(22)
C(19)-C(24)-C(23)	115.8(16)	115.0(18)

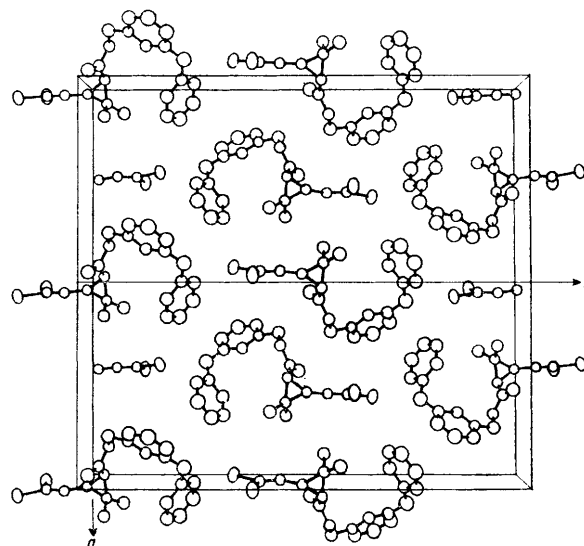
TABLE 3 (Continued)

(c) Selected intermolecular contacts

	(I)	(II)
O(9) ··· H(3 <sup>II</sup> )	2.71	2.66
O(10) ··· HA(11 <sup>III</sup> )	2.92	2.90
O(18) ··· H(22 <sup>III</sup> )	2.81	2.79
H(2) ··· HB(6 <sup>IV</sup> )	2.91	2.89
H(3) ··· HA(5 <sup>V</sup> )	2.88	2.85
HA(5) ··· HB(6 <sup>IV</sup> )	2.72	2.70
HA(6) ··· H(24 <sup>VI</sup> )	2.76	2.68
HC(6) ··· H(24 <sup>VI</sup> )	2.68	2.61
H(15) ··· H(20 <sup>I</sup> )	2.73	2.62
H(20) ··· H(22 <sup>III</sup> )	2.85	2.90

Roman numeral superscripts refer to the following equivalent positions, related to the reference molecules at  $x, y, z$ :

I	$x, y, -1 + z$	IV	$-\frac{1}{2} - x, -y, -\frac{1}{2} + z$
II	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	V	$-\frac{1}{2} - x, -y, \frac{1}{2} + z$
III	$\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$	VI	$x, y, z + 1$

FIGURE 2 Contents of two unit cells of (I), viewed parallel to the  $c$  axis

## DISCUSSION

Comparison of the packing diagrams shows clearly that the molecules of (I) and (III) take up very different conformations and also different positions and orientations in the unit cell. There seems to be no obvious reason why the cell dimensions should be so similar, or even why the two compounds should crystallise in the same space group, in view of the different shapes of the molecules which are packing together. The molecule of (I) is relatively more compact than that of (III). This is caused by major changes in the torsion angles about the three unfixed bonds in the 3-phenoxybenzyl groups (see Table 4). It seems therefore, that there is no preferred conformation for this end of the molecule in the solid state.

In (III), it is the hydrogen atom H(11) which is very close (0.05 Å) to the plane of the benzyl group, whereas in (I), O(10) is close [0.07(1) Å] to this plane.

The torsion angles about the three bonds in the ester group linkage are similar in both (I) and (III); the C(8)-O(9) bond is pointing towards the axis of the cyclopropane ring, with C(7) and C(11) disposed *s-trans* about

TABLE 4

Torsion angles ( $^{\circ}$ ) and mean planes for (I), (II), and (III) <sup>a</sup>

(a) Torsion angles				
	(I)	(II)	(III)	
C(1)–C(2)–C(3)–C(4)	–148(1)	–146(2)	–90(5)	
C(1)–C(2)–C(3)–C(7)	141(2)	141(2)	–161(4)	
C(3)–C(7)–C(8)–O(9)	41(2)	36(3)	39(6)	
C(4)–C(7)–C(8)–O(9)	–30(3)	–36(3)	–36(6)	
O(9)–C(8)–O(10)–C(11)	5(2)	6(2)	7(5)	
C(8)–O(10)–C(11)–C(12)	93(2)	95(2)	104(3)	
C(8)–O(10)–C(11)–HA(11)	–30	–26	–13	
O(10)–C(11)–C(12)–C(13)	7(2)	3(2)	–106(3)	
C(13)–C(14)–O(18)–C(19)	–30(2)	–27(3)	–136(3)	
C(14)–O(18)–C(19)–C(24)	–55(2)	–56(2)	21(5)	

(b) Deviations ( $\text{\AA}$ ) from mean planes. Atoms italicised were used to define the plane

	(I)	(II)	(III)
Plane (1)			
<i>X(1)</i>	–0.000(2)	0.004(6)	–0.004(4)
<i>X(2)</i>	–0.004(2)	–0.003(5)	0.006(4)
<i>C(1)</i>	0.004(14)	–0.007(15)	0.006(30)
<i>C(2)</i>	0.004(14)	0.015(16)	–0.022(38)
<i>C(3)</i>	–0.004(15)	–0.009(17)	0.014(32)
<i>C(4)</i>	–0.661(15)	–0.675(18)	–1.174(29)
<i>C(7)</i>	0.826(16)	0.808(19)	–0.433(31)
Plane (2)			
<i>C(7)</i>	0.004(15)	–0.001(16)	–0.001(30)
<i>C(8)</i>	–0.014(15)	0.005(18)	0.004(38)
<i>O(9)</i>	0.006(11)	–0.002(13)	–0.002(23)
<i>O(10)</i>	0.004(9)	–0.001(11)	–0.001(20)
<i>C(3)</i>	–0.832(13)	–0.764(17)	0.786(30)
<i>C(4)</i>	0.663(14)	0.716(16)	–0.701(27)
<i>C(11)</i>	0.155(16)	0.120(18)	–0.167(28)
HA(11)	–0.22	–0.21	–0.04
HB(11)	–0.33	–0.42	0.836(29)*
<i>C(12)</i>	1.576(15)	1.512(17)	–1.505(27)
Plane (3)			
<i>C(11)</i>	–0.041(17)	–0.020(19)	–0.079(27)
<i>C(12)</i>	0.025(15)	0.008(17)	0.049(28)
<i>C(13)</i>	0.031(15)	0.018(17)	0.063(31)
<i>C(14)</i>	0.014(16)	0.027(20)	0.010(27)
<i>C(15)</i>	–0.021(20)	–0.006(20)	–0.030(32)
<i>C(16)</i>	–0.007(20)	–0.009(21)	–0.026(29)
<i>C(17)</i>	0.016(18)	0.007(20)	0.040(31)
<i>O(13)</i>	–0.018(12)	–0.024(14)	–0.027(24)
<i>O(10)</i>	0.069(9)	0.031(11)	–1.445(20)
HA(11)	0.64	0.73	0.05
HB(11)	–0.91	–0.83	0.851(29)*
<i>C(19)</i>	0.567(16)	0.470(19)	0.728(28)
Plane (4)			
<i>O(18)</i>	0.030(12)	0.021(14)	–0.024(25)
<i>C(19)</i>	–0.041(15)	–0.023(18)	0.015(29)
<i>C(20)</i>	0.001(16)	–0.011(21)	0.024(33)
<i>C(21)</i>	0.003(19)	0.011(21)	–0.021(30)
<i>C(22)</i>	0.001(18)	0.001(23)	0.006(36)
<i>C(23)</i>	0.020(17)	0.007(20)	–0.014(35)
<i>C(24)</i>	0.014(17)	–0.006(20)	0.014(35)
<i>C(14)</i>	–0.880(16)	–0.909(19)	0.346(27)

(c) Dihedral angles ( $^{\circ}$ ) between planes

Planes	(I)	(II)	(III)
(1)–(2)	114	116	35
(1)–(3)	137	134	90
(1)–(4)	115	116	92
(2)–(3)	81	80	78
(2)–(4)	11	10	126
(3)–(4)	73	72	124

\* Deviation of the carbon of the CN group bonded to C(11) in (III).

the C(8)–O(10) bond. However, there is a small but significant difference in the torsion angles about the

† Note added in proof: The structure of the *p*-bromoanilide derivative of (+)-*trans*-chrysanthemic acid has recently been reported, and confirms the absolute configuration deduced from chemical considerations (A. F. Cameron, G. Ferguson, and C. Hannaway, *J.C.S. Perkin II*, 1975, 1567).

O(10)–C(11) bond. This means that for (I), neither of the hydrogen atoms on C(11) are close to the ester plane, which was the case for (III). However, the plane of the ester group does include both C(11) and the midpoint of the C(3)–C(4) bond in both (I) and (III).

A further difference between (I) and (III) occurs at the other end of the molecules. The plane of the dibromovinyl group almost includes the midpoint of the C(4)–C(7) bond in (I), whereas in (III) the torsion angle about C(2)–C(3) is *ca.* 60° greater, to move the bromine atoms away from the ester group. This indicates some degree of flexibility in this part of the molecule.

The crystal structures of the pyrethroids determined to date show that there is a certain degree of flexibility at each end of the molecules, with the ester linkage in the middle forming a fairly rigid entity. This supports the conclusions drawn from the chemical and biological studies concerning the importance of the rigid ester linkage in the pyrethroids.<sup>5</sup>

Although more data is obviously needed, especially on the conformation in solution, the lack of close intermolecular contacts in the crystal structures so far determined, indicates that these features may carry over to the dissolved insecticide molecules.†

## EXPERIMENTAL

*Crystal Data.*—(I). C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>Br<sub>2</sub>, *M* = 480.2. Orthorhombic needles, *a* = 12.177(4), *b* = 26.707(9), *c* = 6.146(5) Å, *U* = 1 999 Å<sup>3</sup>, *D<sub>m</sub>* (floatation) = 1.57 g cm<sup>–3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.59 g cm<sup>–3</sup>, *F*(000) = 960. Space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (*D*<sub>2</sub><sup>h</sup>, No. 19) uniquely determined. No molecular symmetry required. Mo-*K*<sub>α</sub> radiation, Zr filter, λ = 0.7107 Å; μ(Mo-*K*<sub>α</sub>) = 40.32 cm<sup>–1</sup>. No absorption correction applied.

(II). C<sub>21</sub>H<sub>20</sub>O<sub>3</sub>Cl<sub>2</sub>, *M* = 391.3. Orthorhombic needles *a* = 12.168(16), *b* = 26.577(22), *c* = 6.006(4) Å, *U* = 1 942 Å<sup>3</sup>, *D<sub>m</sub>* (floatation) = 1.33 g cm<sup>–3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.34 g cm<sup>–3</sup>, *F*(000) = 816. Space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (*D*<sub>2</sub><sup>h</sup>, No. 19) uniquely determined. No molecular symmetry required. Cu-*K*<sub>α</sub> radiation, Ni filter, λ = 1.5418 Å, μ(Cu-*K*<sub>α</sub>) = 31.96 cm<sup>–1</sup>. No absorption correction applied.

*Data Collection.*—(I). A crystal of dimensions 0.17 × 0.17 × 0.76 mm was mounted on a Picker four-circle diffractometer. The orientation matrix and cell dimensions were refined using the positions of 12 reflections. Intensity data were collected by θ–2θ scans at 0.5° min<sup>–1</sup>, from 2θ<sub>calc.</sub>(*K*<sub>α1</sub>) – 0.5 to 2θ<sub>calc.</sub>(*K*<sub>α2</sub>) + 0.6°. Stationary-crystal-stationary-counter background counts were taken for 25 s each after the scans. The intensities of all reflections with 2θ ≤ 36° and positive *l* were measured. A reference reflection (581) was measured every 25 reflections. The value of its intensity was plotted against its sequence no. in the data collection, a smooth curve drawn through the points and the data then scaled to this line. This showed a mean reduction in intensity, *I*, of 4% over the entire data collection. Lorentz and polarisation factors (*LP*) were applied and the standard deviations calculated from the formula: σ<sup>2</sup>(*F*) = σ<sup>2</sup>(*I*)/4.*LP*.*I*, where σ<sup>2</sup>(*I*) = total count + (0.25 background) (scan time/background time)<sup>2</sup>. Of 3 129 reflections measured, 361 were considered unobserved

<sup>5</sup> M. Elliott and N. F. Janes, 'Pyrethrum, the Natural Insecticide,' ed. J. E. Casida, Academic Press, New York, 1973, p. 55.

because either  $I < 2\sigma(I)$  or  $I < 80$  counts, in which case it was reset to 40. Averaging of equivalent reflections resulted in 1 564 reflections in the two octants  $hkl$  and  $\bar{h}\bar{k}l$ , of which 1 342 were considered observed. The structure solution and initial refinement were carried out on the 721 reflections considered observed in the  $hkl$  octant.

(II). A crystal of dimensions  $0.02 \times 0.11 \times 0.48$  mm was used for the collection of intensity data on films. The crystal was mounted about  $c$  and Weissenberg photographs for the  $h\bar{k}0$ —4 layers obtained by the multiple-film equi-inclination method. Cell dimensions were calculated from accurately measured precession photographs. The Weissenberg photographs were scanned by the S.R.C. Microdensitometer Service at the Atlas Computer Laboratory, Chilton. Equivalent forms were averaged and the intensities of 518  $hkl$  reflections returned. Intensity values were then checked qualitatively against the films. A few reflections with measured values could not be seen on the top film of a pack, and were rejected. Several spots on the films did not have intensity values measured by the scanner owing to either bad interfilm agreement or misalignment of the crystal, the latter particularly leading to the omission of some strong spots close to the centre line on upper layers. These spots were estimated visually and scaled to the other reflections in the layer. All unmeasured reflections left after this were classed as unobserved. This resulted in a total of 1 035 reflections, with 545 observed. Lorentz and polarisation factors were applied but no interlayer scaling was carried out at this stage.

*Structure Determination.*—(I). A three-dimensional Patterson map enabled location of the bromine atoms and a Fourier map phased by these gave the positions of 10 other atoms. These positions were refined and a further Fourier map enabled location of the remaining 14 non-hydrogen atoms. A weighting scheme which gave a constant  $\langle w\Delta^2 \rangle$  for ranges of  $|F_o|$  gave satisfactory refinement. The bromine atoms were allowed to refine with anisotropic temperature factors and this gave  $R$  0.061 9 for the 721 reflections used.

At this stage the absolute configuration was sought by two structure-factor calculations on the 1 342 observed reflections in both the  $hkl$  and  $\bar{h}\bar{k}l$  octants. The isomer used so far gave  $R$  0.064 3 whereas the isomer obtained by reversing the signs of all three co-ordinates of each atom gave  $R$  0.055 4. The second isomer was thus taken as the correct one and refined to  $R$  0.054 9. The agreement between  $|F_o|$  and  $|F_c|$  was poorest for the low  $\sin \theta/\lambda$  reflections; a difference map showed regions of high electron-density in positions near those calculated for hydrogen atoms from geometrical considerations. The positions of all except the methyl hydrogen atoms were calculated and included in the model. The non-hydrogen atoms were refined and a difference-Fourier map was calculated. The methyl hydrogen atoms were located from this map, included in the model, and the non-hydrogen atoms refined.

For the final refinement, all hydrogen-atom positions were recalculated and given fixed isotropic temperature factors of  $U_{\text{iso}} 0.05 \text{ \AA}^2$  and the weighting scheme used was:  $|F_o| \leq 9.5, w = 1/1.39, |F_o| > 9.5, w = 1/(1.294 - 0.008 57 |F_o| +$

$0.001 98 |F_o|^2)$ . This refinement gave  $R$  0.043 8 and  $R'$  0.057 1 for the 721 observed reflections in the  $hkl$  octant. The maximum change-to-error ratio on the last cycle was 0.053. A weighting analysis showed no obvious trends against ranges of  $\sin \theta/\lambda$  or  $|F_o|$ . The difference map after this refinement showed only peaks attributable to the inadequate description of the thermal motion of the atoms. Measured and calculated structure factors for both (I) and (II) are listed in Supplementary Publication No. SUP 21699 (10 pp., 1 microfiche).\*

(II). Comparison of the diffraction photographs of (I) and (II) showed them to be isomorphous, so the final co-ordinates of the non-hydrogen atoms of (I) were used as a starting model for the solution of the structure of (II). A refinement of this model with all atoms isotropic converged to  $R$  0.101 9, with unit weights. However, agreement between  $|F_o|$  and  $|F_c|$  was poorest for largest  $|F_o|$ , the observed values being very much smaller than the calculated. The high  $|F_o|$  reflections were therefore down-weighted using a three degree polynomial expression and this led to satisfactory refinement later on. Since the five layer scale-factors were refined in the least-squares program, it was necessary to fix them in the cycles in which refinement of the chlorine atoms with anisotropic thermal parameters was carried out. This refinement gave  $R$  0.082 8 and was followed by a difference Fourier map. This showed regions of high electron-density in positions near those for the hydrogen atoms calculated from geometrical considerations. The positions of all except the methyl hydrogen atoms were calculated and included in the model and the non-hydrogen atoms refined. A further difference map then showed the location of one hydrogen atom on each methyl carbon sufficiently well to allow location of the other two by geometrical considerations. The hydrogen atoms were included with fixed isotropic temperature factors of  $U_{\text{iso}} 0.05 \text{ \AA}^2$ , and refinement of the non-hydrogen atoms then gave final values of  $R$  0.069 0 and  $R'$  0.081 6 for the 545 observed reflections. The final weighting scheme used was:  $|F_o| \leq 11.0, w = 1/4.0, |F_o| > 11.0, w = 1/(-3.843 + 1.111|F_o| - 0.052 8|F_o|^2 + 0.000 784|F_o|^3)$ . The maximum change-to-error in the last cycle was 0.065. A weighting analysis showed no obvious trends against ranges of  $\sin \theta/\lambda$  or  $|F_o|$ . A final difference map showed no peaks  $> 0.35 \text{ e\AA}^{-3}$ .

*Computing.*—The orientation matrix and cell dimension refinement for (I) were carried out on an IBM 1130 computer as were the structure solution, refinement, and molecular geometry calculations by use of the X-RAY ARC programs.<sup>6</sup> Final full-matrix least-squares refinement was done by use of NUCLS,<sup>7</sup> and bond lengths and angles, with errors from the variance-covariance matrix were calculated by use of ORFFE.<sup>7</sup> ORTEP<sup>7</sup> was used to draw the diagrams. Scattering factor curves for non-hydrogen atoms were taken from ref. 8, and for hydrogen from ref. 9; anomalous dispersion coefficients for bromine were taken from ref. 10.

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\* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1975, Index issue.

<sup>6</sup> 'World List of Crystallographic Computer Programs.' *J. Appl. Cryst.*, 1973, **6**, 309.

<sup>7</sup> ICL 4/70 Programs adapted from the IBM 360 versions: NUCLS, R. J. Doedens and J. A. Ibers; ORFFE, W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP, C. K. Johnson.

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<sup>9</sup> R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

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